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Calculation Notes in Support of Ammonia Releases from Waste Tank Ventilation Systems

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Abstract: Ammonia is generated in waste tanks via the degradation of nitrogen compounds. The ammonia is released from the liquids by a mechanism which is dependent on temperature, pH, ionic strength and ammonia concentration. The release of ammonia to the environment occurs via diffusion of ammonia through a stagnant air mass and into the ventilation system.

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Diffusion of Ammonia into The Head Spaces for both Single and Double Shelled Tanks

Purpose: This document reports the results of analyses designed to predict the concentration of ammonia in forced ventilation exhaust gases under normal operating conditions. All data and tank specific information was obtained from document number WHC-SD-BIO-001 REV A.

Methodology: Actively vented single and double shell tanks are vented in a manner such that ventilation flow enters the tank through ventilation headers and exits through an exhaust manifold which is maintained at a reduced pressure. Stream lines for this type of flow typically are smooth and are not highly turbulent with the possible exception of entrance and outlet effects. Assuming nonturbulent flow, diffusion of ammonia from the surface of the tank waste can be represented by a diffusion cell model.

The basis for this analysis is the Arnold diffusion cell. The diffusion height is defined to be the space between the top of the waste surface and the top of the tank. Table 1 lists the critical tank dimensions for the single shell tanks.

TABLE 1
TABLE OF VARIABLES
(single shell tanks)

Diameter (m)	Total Height (m)	Depth of Liquid(m)	Head Space Height (diffusion length)
23 m	11.3 m	5.2 m (nominal operation)	6.1 m (nominal operation)
23 m	11.3 m	9.4 m (Maximum operation)	1.9 m (Maximum operation)

Table 2 lists the critical tank dimensions for the double shell tanks. Data on the heights and nominal capacities for the double shell tanks were taken from Table 2-20 of document WHC-SD-WM-BIO-001. The highest and lowest values were used to calculate the upper and lower bounds for the nominal and maximum capacity cases.

TABLE 2
TABLE OF VARIABLES
(double shell tanks)

Diameter (m)	Total Height (m)	Depth of Liquid(m)	Head Space Height (diffusion length)
23 m	14.25 m	9.1 m (nominal low operation)	5.15 m (nominal operation)
23 m	14.25 m	10.6 m (nominal high operation)	3.65 m (nominal operation)
23 m	14.25 m	9.2 m (maximum low operation)	5.05 m (maximum operation)
23 m	14.25 m	10.7 m (maximum high operation)	3.55 m (maximum operation)

Background:

The basic relation describing the unidirectional diffusion of a gas describes the molar flux relative to a molar-average velocity, J_A . An empirical relation, which is the basis for all, one directional analyses is Fick's law of diffusion (Fick's First Law). For isothermal, isobaric conditions, the Fick rate equation can be stated as:

$$J_{A,z} = -D_{AB} \frac{dc_A}{dz} \quad (1)$$

where $J_{A,z}$ is the molar average flux in the z direction relative to the molar average velocity, D_{AB} is the diffusion coefficient and c_A is the molar concentration.

For nonisobaric, nonisothermal conditions a more general flux relation was proposed by de Groot¹. The de Groot relation is stated as:

$$Flux = - \left(\frac{overall}{density} \right) \left(\frac{diffusion}{coefficient} \right) \left(\frac{concentration}{gradient} \right) \quad (2)$$

expressed in mathematical terms

$$J_A = -C D_{AB} \frac{dy_A}{dz} \quad (3)$$

where y_A is the mole fraction of component A.

For a binary system the unidirectional flux of component A in the z direction relative to the molar average flux can be defined as

$$J_{A,z} = C_A (v_{A,z} - V_z) \quad (4)$$

where $v_{A,z}$ is the velocity of component A in the z direction and V_z is the molar average velocity.

Equating equations 3 and 4 yields the expression

$$\begin{aligned} J_{A,z} &= C_A (v_{A,z} - V_z) \\ &= -C D_{AB} \frac{dy_A}{dz} \end{aligned} \quad (5)$$

solving for $C_A v_{A,z}$ yields

$$C_A v_{A,z} = -C D_{AB} \frac{dy_A}{dz} + C_A V_z \quad (6)$$

for a binary system the molar average velocity can be expressed as

$$C_A V_z = y_A (C_A v_{A,z} + C_B v_{B,z}) \quad (7)$$

The molar flux of component A can then be written as

$$C_A v_{A,z} = -C D_{AB} dy_A/dz + y_A (C_A v_{A,z} + C_B v_{B,z}) \quad (8)$$

considering the diffusion relative to a stationary set of axes define

and

$$N_A = C_A v_A$$

$$N_B = C_B v_B$$

The molar diffusion expression can then be written as

$$N_{A,z} = -C D_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z}) \quad (9)$$

For diffusion into a stagnant system, $N_{B,z}$ is taken to be 0. Rearranging equation 9 and solving for $N_{A,z}$ the defining equation for the molar diffusion of a gas A into B (air) is

$$N_{A,z} = -C \frac{D_{AB}}{1 - y_A} \frac{dy_A}{dz} \quad (10)$$

integrating

$$N_{A,z} \int_{z_1}^{z_2} dz = C D_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - y_A} \quad (11)$$

evaluated at the limits

$$N_{A,z} = \frac{C D_{AB}}{(z_2 - z_1)} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})} \quad (12)$$

Where y_{A1} and y_{A2} are mole fractions of component A at points z_1 and z_2 respectively. For a two component system, component B can be expressed in terms of component A as:

$$1 - y_{A1} = y_{B1}$$

$$1 - y_{A2} = y_{B2}$$

so that the log term can be expressed in terms of component B (air) as

$$\ln \frac{(1 - y_{A2})}{(1 - y_{A1})} = \ln \frac{y_{B2}}{y_{B1}} \quad (13)$$

The log- mean average concentration is defined by the relation

$$y_{B,1m} = \frac{y_{B2} - y_{B1}}{\ln\left(\frac{y_{B2}}{y_{B1}}\right)} \quad (14)$$

the term $\ln(y_{B2}/y_{B1})$ then can be expressed as

$$\ln\left(\frac{y_{B2}}{y_{B1}}\right) = \frac{y_{B2} - y_{B1}}{y_{B,1m}} \quad (15)$$

Equation 15 can be stated in terms of the partial pressure of component A (p_A), component B (p_B) and the system pressure by making the following substitutions:

$$y_A = p_A/P$$

$$y_B = p_B/P$$

$$c = n/V$$

$$n = PV/RT$$

On making the above substitutions, the system pressure cancels out of the partial pressure terms and the expression for the steady state diffusion (molar flux), of component A into a stagnant gas (B) reduces to

$$N_{A,z} = \frac{D_{AB} P}{R T (z_2 - z_1)} \frac{(p_{A1} - p_{A2})}{p_{B,1m}} \quad (16)$$

$z_2 - z_1$ is the diffusion length, which in this analysis is taken to be the length of the vapor space above the liquid. Pressure p_{A1} is the equilibrium vapor pressure of component A at the liquid/air interface and P is the system pressure, taken to be one atmosphere in this analysis. The values of p_{B1} and p_{B2} are the partial pressures of air in this analysis and are obtained from the ammonia values p_A using the relation

$p_{B1} = 1 - p_{A1}$ where the partial pressures are expressed in atmospheres. The value for p_{B2} is obtained in a similar manner.

The diffusion constant, D_{AB} has units of cm^2/sec and was calculated based on an empirical estimation method presented by Fuller, Schettler and Giddings².

M_A and M_B are the molecular weights of ammonia and air respectively, P is the system pressure in atmospheres and T is the temperature in $^{\circ}\text{K}$

$$D_{AB} = \frac{10^{-3} T^{1.75} \left[\frac{(M_A + M_B)}{M_A M_B} \right]^{1/2}}{P \left[(\sum v)_A^{1/3} + (\sum v)_B^{1/3} \right]^2} \quad (17)$$

The terms $(\sum v)_A$ and $(\sum v)_B$ are defined as diffusion volumes and were obtained from Table 3-342 of Perry's Chemical Engineers Handbook². The values for air and ammonia are listed below

$$(\sum v)_A = 14.9 \quad (\text{NH}_3)$$

$$(\sum v)_B = 20.1 \quad (\text{air})$$

For $T = 372^\circ\text{K}$ (210°F) and one atmosphere pressure the diffusion constant of ammonia in air is

$$D_{AB} = \frac{10^{-3} 372^{1.75} \left[\frac{(17.03 + 28.84)}{(17.03)(28.84)} \right]^{1/2}}{(1) \left[(14.9)^{1/3} + (20.1)^{1/3} \right]^2} \quad (18)$$

$$D_{AB} = 0.3571 \text{ cm}^2/\text{sec}$$

System Specific Calculations:

Assumptions:

The concentration of ammonia in the headspace air was calculated for both the single and double shell tanks. The tank parameters required for the calculations were the diameter and diffusion length, these parameter are listed in tables 1 and 2 of this document.

It is reported in section 5.3.3.9.1 of document number WHC-SD-WM-B10-001 that the equilibrium vapor concentration of ammonia in waste tanks is 0.4mg/liter of headspace volume. It is further stated that the concentration of ammonia in the headspace does not change with pH at pH's above 9.27. At a concentration of 0.4 mg/L, the partial pressure of ammonia is 0.00072 Atm. at 372 °K.

Calculations:

$$\begin{aligned} 0.4 \text{ mg/l} * \frac{1}{1000} * \text{g/mg} * \frac{1}{17 \text{ g/g-mole}} * 22.4 \text{ l/g-mole} * \frac{372}{273} \\ = 0.00072 \frac{\text{liter NH}_3}{\text{liter headspace volume}} \quad (19) \end{aligned}$$

Letting $p_A = p_{\text{NH}_3} = 0.00072 \text{ atm.}$

$$p_B = 1 - p_A = 1 - 0.00072 = 0.9993 \text{ atm.}$$

$$P_t * \frac{V_{NH_3}}{V_{tot}} = P_{NH_3} \quad (20)$$

$$\begin{aligned} P_{B1m} &= \frac{1 - 0.9993}{\ln\left(\frac{1}{0.9993}\right)} \\ &= \frac{0.00072}{\ln 1.0007} \\ P_{B1m} &= 1.029 \quad (21) \end{aligned}$$

$$\begin{aligned} N_{Az} &= \frac{0.357 \frac{cm^2}{sec}}{(0.08205) \frac{l \cdot atm}{^\circ K \cdot mole} (372 \text{ } ^\circ K) (610 \text{ cm})} * \frac{1 \text{ atm} * 0.00072 \text{ atm}}{1.029 \text{ atm} * 1000 \frac{cm^3}{l}} \\ &= 1.43 \times 10^{-11} \frac{g \cdot mole}{cm^2 \cdot sec} \quad (22) \end{aligned}$$

Using the data from Table 1 (nominal operation):

The molar diffusion will then be

for a surface area of $4.15 \times 10^6 \text{ cm}^2$ the mass release rate of ammonia in the vented headspace air will be

$$\begin{aligned} 1.43 \times 10^{-11} \frac{g \cdot mole}{cm^2 \cdot sec} * 4.15 \times 10^6 \text{ cm}^2 * 17 \frac{g}{g \cdot mole} &= 1.01 \times 10^{-3} \frac{g}{sec} \\ (3.6 \frac{g}{hr}) \quad (23) \end{aligned}$$

All headspace concentrations were calculated in a similar manner, only the diffusion length differed. The results are tabulated in Table 3.

TABLE 3
Concentration of Ammonia in the
Headspace for Selected Double Shell and
Single Shell Tanks

Tank Type	Diameter (m) (surface area cm ²)	Total Height (m)	Depth of Liquid (m)	Diffusion Path Length (m)	Ammonia Release Rate (g/hr)
SS	²³ 4.15 x 10 ⁶	11.3	5.2	6.1	3.6
SS	²³ 4.15 x 10 ⁶	11.3	9.4	1.9	11.6
DS	²³ 4.15 x 10 ⁶	14.25	9.1	5.15	4.3
DS	²³ 4.15 x 10 ⁶	14.25	10.6	3.65	6.0
DS	²³ 4.15 x 10 ⁶	14.25	9.2	5.05	4.4
DS	²³ 4.15 x 10 ⁶	14.25	10.7	3.55	6.2

Turbulent flow considerations:

Because of momentum considerations, the flow across the top of tank is never truly streamlined. The incoming air mass tumbles into the tank for a certain distance before flowing toward the exit port, which is maintained at a reduced pressure. Although it is technically possible to calculate the free volume of a tank that is swept by the incoming air mass the uncertainties in such a calculation would be quite high.

Using engineering judgement, it is reasonable to assume that there is some fraction of the free volume of a waste tank that is stagnant. If it can be assumed that at least one meter of tank atmosphere above the liquid surface is stagnant the maximum release rate of ammonia into the vent gas system for the forced ventilation case is approximately 16 grams per hour per tank for any double or single shell tank.

REFERENCES

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2. E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, 58(5), 18 (1966).
3. R. H. Perry, D. W. Green, *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw-Hill Book Co., 1984.
4. WHC-SD-WM-BIO-001 REV A, Tank Waste Remediation System, "Basis for Interim Operation", (Draft).

CHECKLIST FOR TECHNICAL PEER REVIEW

Document Reviewed: WHC-SD-WM-CN-068 REV 0

Scope of Review: *Peer review entire document*

Yes No NA

☐	☐	☒	Previous reviews complete and cover analysis, up to scope of this review, with no gaps.
☒	☐	☐	Problem completely defined.
☐	☐	☒	Accident scenarios developed in a clear and logical manner.
☒	☐	☐	Necessary assumptions explicitly stated and supported.
☐	☐	☒	Computer codes and data files documented.
☒	☐	☐	Data used in calculations explicitly stated in document.
☒	☐	☐	Data checked for consistency with original source information as applicable.
☒	☐	☐	Mathematical derivations checked including dimensional consistency of results.
☒	☐	☐	Models appropriate and used within range of validity or use outside range of established validity justified.
☒	☐	☐	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
☐	☐	☒	Software input correct and consistent with document reviewed.
☐	☐	☒	Software output consistent with input and with results reported in document reviewed.
☒	☐	☐	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
☐	☐	☒	Safety margins consistent with good engineering practices.
☒	☐	☐	Conclusions consistent with analytical results and applicable limits.
☒	☐	☐	Results and conclusions address all points required in the problem statement.
☒	☐	☐	Format consistent with appropriate NRC Regulatory Guide or other standards
☒	☐	☐	Review calculations, comments, and/or notes are attached.
☐	☐	☐	Document approved.

D. L. Scott

David L. Scott

8/29/96

Reviewer (Printed Name and Signature)

Date

Any notes and/or comments should be attached.